SUPPLEMENTARY REPORT
For the
CHEROKEE NATION'S
AIR TOXICS MONITORING PROJECT
AT CHEROKEE HEIGHTS,
NEAR PRYOR, OKLAHOMA
SEPTEMBER, 2006 TO MARCH, 2008

Prepared by the
Cherokee Nation Environmental Programs
P. O. Box 948
Tahlequah, Oklahoma 74465

As a Supplement to the Final Project Report
Produced by Eastern Research Group (ERG)
601 Keystone Park Drive
Suite 700
Morrisville, North Carolina 27560

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COMMUNITY AIR TOXICS PROJECT
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Abstract

The Cherokee Nation's Environmental Programs (CNEP) collected 93 air samples (including nine duplicate samples) for VOC analyses at its Cherokee Heights ambient air monitoring station near Pryor, Oklahoma from September 26, 2006 to March 31, 2008. The samples were 24-hour time-weighted average samples collected in 6-liter vacuum canisters on a 1-in-6 day sampling schedule. Each sample was analyzed for a suite of 60 volatile organic compounds (VOCs) by means of EPA Test Method TO-15 by Eastern Research Group (ERG) in North Carolina. Sample data were analyzed by both CNEP and ERG. ERG entered all sample data into the U. S. Environmental Protection Agency's (EPA) Air Quality System (AQS) on-line database.

Ninety-three valid samples were collected during this project. Fourteen to thirty VOCs were detected in each sample. VOC concentrations were compared to EPA Region 6 Human Health Screening Levels (including chronic inhalation toxicity values), Oklahoma Department of Environmental Quality (ODEQ) Maximum Acceptable Ambient Concentrations (MAACs), and Agency for Toxic Substances and Disease Registry (ATSDR) Minimal Risk Levels (MRLs). Only 8 VOCs exceeded one or more of these health-based benchmarks in one or more of the 93 valid samples. Only one of these eight VOCs (acrolein) exceeded an ATSDR MRL or an ODEQ MAAC more than once. These 8 VOCs were chloromethane, 1,3-butadiene, acrolein, chloroform, 1,2-dichloroethane, benzene, carbon tetrachloride, and trichloroethylene.

ERG used EPA's risk-based screening approach to identify 1,3-butadiene, acrolein, benzene, and carbon tetrachloride as pollutants of interest at Cherokee Heights. ERG performed a risk-based emissions assessment, calculating cancer and non-cancer surrogate risk approximations for hazardous air pollutants at Cherokee Heights. This assessment, using national air toxics assessment (NATA) modeling, revealed that acrolein is the only pollutant of interest that poses an elevated risk of chronic non-cancer effects (such as asthma) to residents of Cherokee Heights. Carbon tetrachloride, for which there is believed to be a global background concentration, poses the highest chronic cancer risk to residents of Cherokee Heights.

Ratios of BTEX compounds (benzene, toluene, ethylbenzene, and xylenes) and the BTEX concentration profile were not characteristic of motor vehicle emissions.

Calculation of Pearson correlation coefficients revealed only weak correlations between concentrations of the four pollutants of interest (1,3-butadiene, acrolein, benzene, and carbon tetrachloride) and meteorological parameters (temperature, relative humidity, wind speed). There were no seasonal trends in VOC concentrations.

Method Detection Limits (MDLs) reported by ERG for some VOCs in samples collected during this project were higher than the EPA Region 6 Human Health Screening Levels to which project data were compared. Thus it is likely that false negatives were reported for VOCs of particular concern in this project. This problem might affect the results for

1,3-butadiene and trichloroethylene, which the lab reported as undetected in many samples.

With respect to VOCs, ambient air quality at Cherokee Heights is about the same, or perhaps slightly better than, ambient air quality in the urban-industrial environment of Tulsa. Acrolein and carbon tetrachloride pose a higher risk at Cherokee Heights than in Tulsa, while benzene and 1,3-butadiene pose a lower risk in Cherokee Heights than in Tulsa.

ERG produced the final report for this project in July, 2008. This Supplementary Report, produced by the CNEP, provides additional information, data tables, and data analyses that supplement ERG's final project report. The final project report and this Supplementary Report have been distributed to the EPA Region 6 office in Dallas, Texas, to the Oklahoma Department of Environmental Quality, and to interested parties within the Cherokee Nation, including the Cherokee Nation Health Administration.

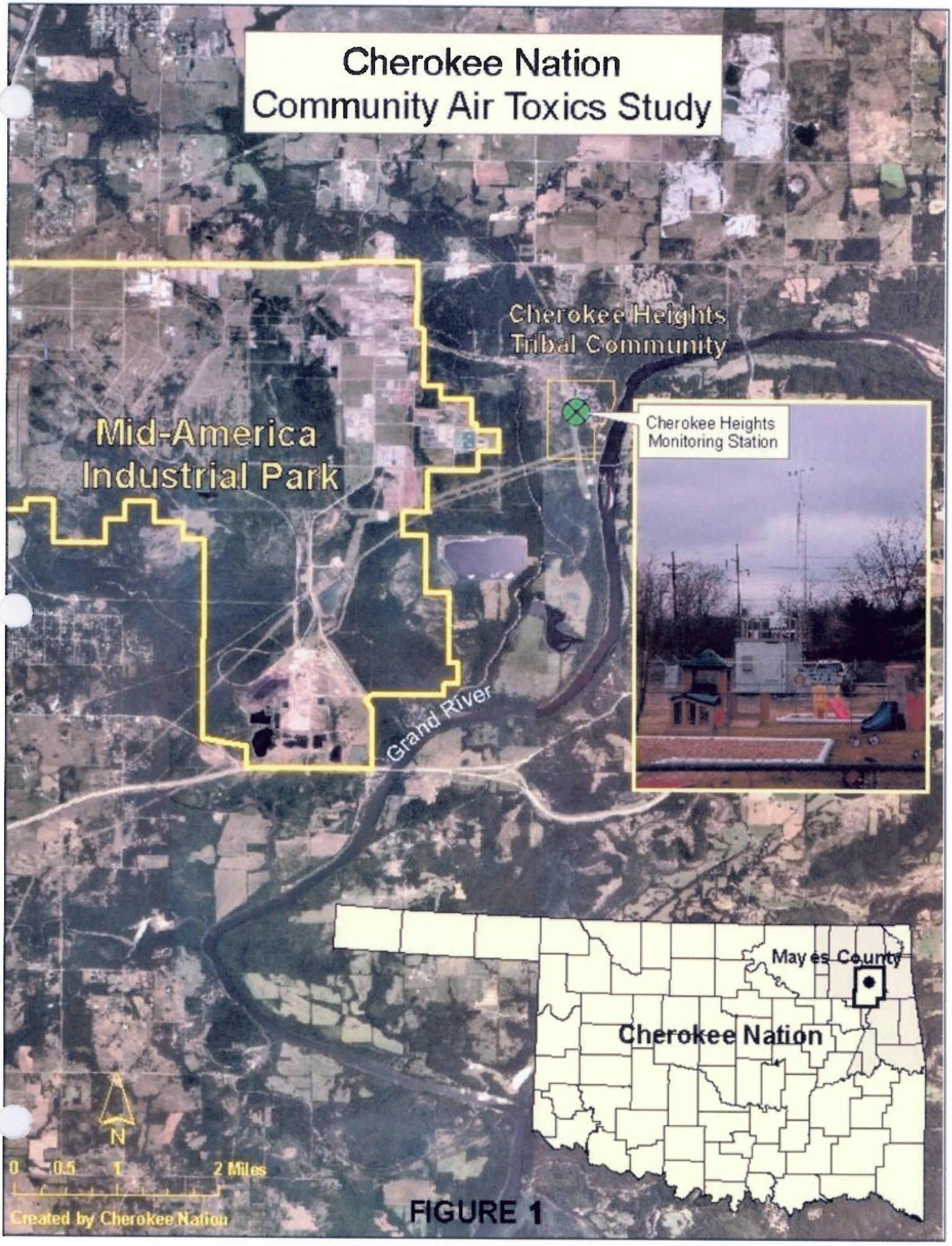
In summary, the CNEP is engaged in a multi-year effort to measure the concentrations of hazardous air pollutants (volatile organic compounds, carbonyl compounds, and metals) in ambient air at the Cherokee Heights tribal housing complex. It has collected eighteen months of data on VOC concentrations; it will begin sampling for metals via EPA Compendium Method IO-3.5 in fiscal year 2009; and it plans to sample for carbonyl compounds via EPA Compendium Method TO-11A when funding becomes available in the future. The resulting data have been, and will be, analyzed to determine the risks posed by such pollutants to the health of residents of Cherokee Heights.

Overview of Project Origin and Purpose

A 9000-acre industrial park is located in Mayes County, Oklahoma. This industrial park is 40 miles east of Tulsa and 30 miles north of Muskogee. Over 70 firms operate within the industrial park, including a coal-fired power plant, a new gas-fired power plant, chemical and plastic industries, paper product industries, and several other industries that emit hazardous air pollutants.

All major point sources of air pollutants in Mayes County are spatially clustered near the industrial park, as are the tribal population centers of Pryor, Chouteau, Locust Grove, Salina, Sportsman Acres, and Cherokee Heights. Cherokee Heights is less than one mile from some sections of the industrial park. The Cherokee Nation has established an ambient air monitoring station (AQS ID number 40-097-9014) on Tribal Trust land at the Cherokee Heights housing complex (**Figure 1**). This monitoring station includes instruments for monitoring criteria pollutants (ozone, sulfur dioxide, nitrogen oxides, and particulate matter), hazardous air pollutants (VOCs and metals), and meteorological parameters (wind speed, wind direction, temperature, relative humidity, and rainfall).

The proximity of the Cherokee Heights tribal housing complex to the industrial park, coupled with the high incidence of respiratory cancer in Mayes County, prompted the Cherokee Nation to conduct a VOC screening project at its Cherokee Heights monitoring


Cherokee Nation
Community Air Toxics Study
Cherokee Heights
Tribal Community
Cherokee Heights
Monitoring Station
Mid-America
Industrial Park
Grand River
Mayes County
Cherokee Nation
N
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Created by Cherokee Nation

FIGURE 1

station during the winter of 2005 (December 23, 2004 to March 29, 2005). Fifteen samples were collected in vacuum canisters and analyzed via GC/MS in accordance with EPA Test Method TO-15. The sampling interval was 1-in-6 days and each sample was a 24-hour time-weighted average sample. The results of the screening project were as follows: (1) 24 of 59 VOCs were detected in one or more samples; (2) 15 of the 24 detected VOCs were hazardous air pollutants (HAPs); (3) only 5 detected VOCs (HAPs) exceeded an EPA Region 6 health-based benchmark in one or more samples, but 4 of these 5 VOCs were respiratory carcinogens (benzene, MTBE, methylene chloride, TCE). Thus the data for this short-term screening project revealed a potential problem with toxic VOCs in ambient air in the Cherokee Heights area.

The findings of the screening project prompted the CNEP to obtain additional EPA funding for a more thorough 18-month VOC sampling project at its Cherokee Heights monitoring station. The remainder of this Supplementary Report describes this 18-month CNEP Air Toxics Monitoring Project (referred to hereinafter as "the project" or as the ATMP).

Sampling and Analysis Methods

The CNEP used an RM Environmental Systems RM910A sampling device, Restek or Graseby 6-liter vacuum canisters, and ⅛-inch diameter 316L stainless steel tubing and fittings to collect samples for this ATMP. ERG performed EPA Compendium Method TO-15 "canister sampling system certifications" (aka, NATTS Certifications) on the RM910A, tubing, and fittings prior to commencement of sample collection and after completion of sample collection. The purpose of this certification was to quantify the potential for the sampler to cause positive or negative bias in VOC concentrations in air samples. ERG performed the initial certification on the CNEP's sampler on December 3-6, 2005, and the final certification on May 11-13, 2008. The sampler passed both NATTS certifications; that is, the certification revealed that the sampler exhibited minimal potential for biasing.

The CNEP performed flow verification checks on its RM910A sampler in accordance with Section 8.3.5 of EPA's *Compendium Method TO-15*. A primary standard (Hastings HBM-1A bubble meter) was used for these flow verification checks. The CNEP performed these flow verification checks before commencement of sample collection, during the sample collection period, and after completion of sample collection. These flow verification checks were performed on July 12, 2006; on January 16, 2008; and on April 9, 2008. The sampler passed each of these three flow verification checks; that is, the flow rate of the sampler was found to be within acceptable limits (±10%) of the flow rate measured by the primary standard.

The sampling equipment was mounted in racks in a climate-controlled shelter at the CNEP's ambient air monitoring station at Cherokee Heights. The inlet for the sampling system was a ⅛-inch diameter 316L stainless steel tube and an inverted glass funnel mounted on the roof of the shelter, approximately twelve feet above ground.

Samples were collected in Restek or Graseby 6-liter stainless steel vacuum canisters. Each canister was cleaned and prepared by ERG for use in sample collection. Each canister had a vacuum of –29 to –30 inches of mercury (in. Hg) prior to sample collection. Single samples were collected at a flow rate of 3.4 cc/min. Duplicate samples were collected at a flow rate of 6.8 cc/min using two canisters and stainless steel tubing with a tee connection. Samples were collected on the same 1-in-6 day schedule used by the EPA for ambient particulate monitoring. The dates for duplicate sample collection were selected by means of a random number table. Ten percent of all samples were duplicate samples. Each sample was a 24-hour time-weighted-average (TWA) sample.

Sample collection began on September 26, 2006 and concluded on March 31, 2008. The Sample Schedule is shown in **Appendix A** of this Supplementary Report. A total of 106 samples, including 13 duplicate samples, was collected. Ninety-three (93) of these samples, including 9 duplicate samples, were valid samples that produced useful data. Thirteen (13) samples, including 4 duplicate samples, were invalid. Thus the data completeness for this project was 87.7% (93 valid samples out of 106 total samples). Samples were declared invalid by the CNEP because of suspected canister leaks (for example, the canister pressure was zero at the conclusion of sample collection) or because the sample collection period was too long (more than 26 hours).

Samples were shipped to ERG for analysis. The chain of custody for each sample was documented in the ERG "Toxics/SNMOC Sample Data Sheet", CNEP "SOP & Field Sample Report Form", and Federal Express airbill that accompanied each sample shipment to ERG. Likewise, the chain of custody for each vacuum canister shipped from ERG to CNEP was documented in the ERG "Toxics/SNMOC Sample Data Sheet" and Federal Express airbill that accompanied each such canister shipment.

ERG analyzed each sample for a suite of 60 VOCs in accordance with procedures described in EPA's *Compendium Method TO-15*, in ERG's Quality Assurance Project Plan, and in *Technical Assistance Document for the National Ambient Air Toxics Trends and Assessment Program, Final Draft* (ERG, May 17, 2004).

ERG reported sample data and quality assurance/quality control (QA/QC) data to the CNEP each month by means of ERG "Certificate of Analysis" forms. The CNEP analyzed the data in these forms, determining which VOCs were detected in each sample and identifying the VOCs present at a concentration in excess of one or more human health risk-based benchmarks. Data were compared to the following benchmarks:

EPA Region 6 Human Health Medium-Specific Screening Levels
  Chronic inhalation toxicity values (non-cancer and cancer values)
  Region 6 Screening values for ambient air
Oklahoma Department of Environmental Quality (ODEQ) Maximum Acceptable Ambient Concentrations (MAACs)
Agency for Toxic Substances and Disease Registry (ATSDR) Minimal Risk Levels (MRLs) for inhalation.

The CNEP analyzed the precision of duplicate samples, calculating the relative percent difference between duplicate concentrations of each VOC. The CNEP also calculated the benzene/toluene ratio in each sample.

After analyzing the data in the ERG "Certificates of Analysis", the CNEP compiled the data into two sets of tables. The tables were created to facilitate the discovery of any seasonal trends or other trends that might exist in VOC concentrations at Cherokee Heights. Each table contained three months of data for a single season. The months included in each season were as follows: Winter (January, February, and March); Spring (April, May, and June); Summer (July, August, and September); and Autumn (October, November, and December). There were two tables for each season. The first table – the "Seasonal Trends" table – showed sample results for all VOCs in each sample collected during a season. The second table – the "Seasonal Statistics" table – showed basic statistics calculated for the data by CNEP. A total of twelve such tables were compiled by the CNEP during this project. These tables are shown in **Appendix B** of this Supplementary Report. These tables are explained and discussed in the Results and Discussion sections of this Supplementary Report.

The CNEP compared sample data for VOCs with meteorological data from its own meteorological instruments at its Cherokee Heights air monitoring station. The CNEP did this in an attempt to determine if VOC concentrations were correlated to wind direction, wind speed, temperature, relative humidity, and precipitation. This was also done in an attempt to determine if detected VOCs might be coming from nearby emissions sources in the industrial park, Locust Grove, and elsewhere.

ERG entered all sample data for this project into the EPA's Air Quality System (AQS) on-line database.

CNEP and ERG performed all work for this project in accordance with EPA-approved Quality Assurance Project Plans (QAPPs). The CNEP QAPP is:

Quality Assurance Project Plan and Work Plan for the Air Toxics Monitoring Project of the Cherokee Nation Environmental Programs, December, 2007; and September, 2006.

The ERG QAPP is:

Support for the EPA National Monitoring Programs (NMOC, UATMP, PAMS, HAPs, and NATTS), Contract No. 68-D-03-049, 2007/2008. *Quality Assurance Project Plan, Category 1.* Eastern Research Group, Inc., Morrisville, North Carolina. The previous version of this QAPP was dated 2004/2005.

Results

Results for all project samples are shown in **Tables 1** through **12** in **Appendix B** of this Supplementary Report.

The six "Seasonal Trends" tables show sample results for all VOCs in each sample collected during a season. Sample dates on weekends and holidays are shown in boldface. Sample concentrations are in micrograms per cubic meter ($\mu g/m^3$). Sample dates with two concentrations indicate duplicate samples. Sample concentrations shown in boldface exceeded an EPA, ATSDR, or ODEQ health-based benchmark described in the Sampling and Analysis Methods section above. Invalid samples are shaded and the reason for invalidation is shown beneath the table.

The six "Seasonal Statistics" tables show basic statistics calculated for the sample data for each season. Statistics were calculated for each VOC that was detected in at least one sample during a season. VOC concentrations that were undetected (flagged ND or U) were set equal to ½ their method detection limit (MDL), then included in the calculation of statistics. The following statistics were calculated for each VOC that was detected: the number of samples in which the VOC was detected during the season; the concentration range (minimum to maximum) of the VOC during the season; the arithmetic mean concentration, standard deviation (S or σ_{n-1}), and coefficient of variation (CV) of each VOC during the season; and the number of samples in which the VOC's concentration exceeded an EPA, ATSDR, or ODEQ health-based benchmark during the season. VOCs exceeding such a benchmark are shown in boldface. A coefficient of variation greater than 1 is shown in boldface. Method detection limits (MDLs), as reported by ERG, and VOC concentrations (mean, range, standard deviation, and CV) are in $\mu g/m^3$.

Fourteen to thirty VOCs were detected in each sample, with the average number of VOCs detected in any given sample being 22.3. The average number of VOCs detected was highest in the autumn of 2006 and in the winter of 2008, when ERG attained its lowest MDLs.

Only 8 VOCs exceeded one or more of the EPA, ATSDR, or ODEQ health-based benchmarks in one or more of the 93 valid samples. Only one of these eight VOCs (acrolein) exceeded an ATSDR MRL or an ODEQ MAAC more than once. These 8 VOCs and their concentration ranges over 93 samples were as follows:

Chloromethane (0.39 to 1.91 $\mu g/m^3$), exceeded an EPA, ATSDR, and/or ODEQ benchmark in 44 samples;

1,3-Butadiene (ND to 0.21 $\mu g/m^3$), exceeded a benchmark in 14 samples;

Acrolein (0.18U to 4.30 $\mu g/m^3$), exceeded a benchmark in 91 samples;

Chloroform (ND to 0.19 $\mu g/m^3$), exceeded a benchmark in 31 samples;

1,2-Dichloroethane (ND to 0.12 $\mu g/m^3$), exceeded a benchmark in only 1 sample;

Benzene (0.17 to 1.09 $\mu g/m^3$, with one anomalously high concentration of 3.81 $\mu g/m^3$) exceeded a benchmark in all 93 samples;

Carbon tetrachloride (0.21 to 1.05 $\mu g/m^3$), exceeded a benchmark in all 93 samples;

Trichloroethylene (TCE) (ND to 0.54 $\mu g/m^3$), exceeded a benchmark in 11 samples.

Duplicate samples showed good precision, with only 2 to 5 VOCs in each pair of samples (primary and duplicate) having a relative percent difference (RPD) greater than 20% or 25%. Results for duplicate samples collected on January 19, 2008 showed less precision, with 9 VOCs having RPDs in excess of 25%. This included acrolein, with an RPD of 69.2%. Results for duplicate samples collected on March 13, 2008 showed relatively poor precision, largely because VOC concentrations (particularly of BTEX compounds) in one of the two samples were anomalously high for no apparent reason. Twelve VOCs in these samples had RPDs in excess of 25%. This included 1,3-butadiene (RPD = 111.1%) and benzene (RPD = 101.8%).

Benzene-toluene ratios ranged from 0.31 to 2.70. The benzene-toluene ratio in one sample (September 27, 2007) was 0.02. With the exception of two samples, these ratios are not characteristic of vehicular (gasoline engine) emissions. The ratios in the samples collected on Friday, May 18, 2007, and on Monday, June 11, 2007 were 0.35 and 0.31 respectively. These two ratios are characteristic of vehicular emissions.

Discussion

ERG used EPA's risk-based screening approach to identify pollutants of interest at Cherokee Heights. This approach is described in the EPA guidance document, *A Preliminary Risk-based Screening Approach for Air Toxics Monitoring Data Sets* (Air, Pesticides, and Toxics Management Division, Atlanta, Georgia, February, 2006). Using this approach, ERG identified four VOCs – acrolein, benzene, carbon tetrachloride, and 1,3-butadiene, which exceeded EPA screening levels – as being VOC pollutants of interest at Cherokee Heights.

ERG compared daily, seasonal, and period (18-month) averages of concentrations for pollutants of interest to EPA human health benchmarks (see Sections 9.0 thru 9.2.1 of ERG's final report for this project). Such comparisons served as surrogates in the approximation of chronic risk posed by such pollutants to the residents of Cherokee Heights. These comparisons revealed that concentrations of acrolein were generally higher at Cherokee Heights than in Tulsa. In contrast, benzene concentrations were generally lower at Cherokee Heights than in Tulsa. Carbon tetrachloride was present at about the same concentrations at Cherokee Heights as at Tulsa, which supports the belief that there is a global background concentration of this VOC. There was no seasonal variation in VOC concentrations. The concentrations of pollutants of interest did not exceed acute or chronic ATSDR MRLs, while only seasonal averages of acrolein exceeded intermediate MRLs.

ERG performed a risk-based emissions assessment, calculating cancer and non-cancer surrogate risk approximations for hazardous air pollutants at Cherokee Heights (see

Sections 9.2.2 and 9.2.3 of ERG's final report for this project). This assessment, using national air toxics assessment (NATA) modeling, revealed that acrolein is the only pollutant of interest at Cherokee Heights that poses an elevated risk of chronic non-cancer effects (such as asthma) to residents of Cherokee Heights. Carbon tetrachloride, for which there is believed to be a global background concentration, poses the highest chronic cancer risk to residents of Cherokee Heights. Arsenic, hexavalent chrome, and benzene are the carcinogenic pollutants emitted in the greatest quantities from sources in the vicinity of Cherokee Heights.

ERG analyzed the ratios of BTEX compounds (benzene, toluene, ethylbenzene, and xylenes) and the BTEX concentration profile for the CNEP's VOC project sample data (see Section 6.0 of ERG's final report for this project). ERG determined from this analysis that sources other than motor vehicles are likely influencing the concentrations of BTEX compounds at Cherokee Heights. This confirms the CNEP's finding that benzene-toluene ratios in ambient air at Cherokee Heights are not characteristic of vehicular emissions.

ERG calculated Pearson correlation coefficients between the four pollutants of interest (1,3-butadiene, acrolein, benzene, carbon tetrachloride) and the following six meteorological parameters: average maximum daily temperature, average daily temperature, average daily dew point temperature, average daily wet bulb temperature, average daily relative humidity, and average wind speed (see Section 8.0 of ERG's final report for this project). ERG found only weak correlations between the concentrations of the four pollutants of interest and wind speed, temperature, and relative humidity. This quantitative analysis confirms the CNEP's qualitative observation that there is no apparent correlation between VOC concentrations and meteorological parameters at Cherokee Heights. Analyses of project data by ERG and CNEP revealed no seasonal trends in VOC concentrations at Cherokee Heights. Qualitative analyses of project data by the CNEP revealed no obvious trends in VOC concentrations on weekends or holidays, when industrial activity in the Cherokee Heights area might be expected to decrease.

Method Detection Limits (MDLs) reported by ERG for some VOCs in samples collected during this project were higher than the EPA Region 6 Human Health Screening Levels to which project data were compared. Thus it is likely that false negatives were reported for VOCs of particular concern in this project. That is, data may falsely show that a particular VOC was not present at a concentration higher than a Screening Level when, in fact, that VOC may actually have been present at a concentration higher than the Screening Level but lower than the MDL achieved by the lab. This limits the usefulness of some project data and forces the CNEP to accept the possibility of false negatives for some VOCs of concern, including 1,3-butadiene, acrolein, carbon tetrachloride, and trichloroethylene. This problem may not affect the results for acrolein and carbon tetrachloride, which exceeded screening levels, respectively, in 91 and 93 of the 93 valid samples. But this problem might affect the results for 1,3-butadiene and trichloroethylene, which the lab reported as undetected in many samples.

With respect to VOCs, ambient air quality at Cherokee Heights is about the same, or perhaps slightly better than, ambient air quality in the urban-industrial environment of Tulsa (see Tables 11, 12, and 13 of ERG's final report for this project). Acrolein and carbon tetrachloride pose a higher risk at Cherokee Heights than in Tulsa, while benzene and 1,3-butadiene pose a lower risk in Cherokee Heights than in Tulsa. The source or sources of acrolein emission in the Cherokee Heights area have not been determined. There is a global background concentration of carbon tetrachloride, so there may be little or nothing that can be done to reduce the risk it poses to human health at Cherokee Heights.

ERG's toxicity-weighted emissions analysis revealed that metals such as lead, cadmium, arsenic, hexavalent chromium, and manganese are present in ambient air at Cherokee Heights (see Section 11.0 of ERG's final report for this project). The CNEP is planning to sample for toxic metals at its Cherokee Heights air quality monitoring station in fiscal year 2009. Such sampling will be done via EPA Method IO-3.5. The resulting sample data will be analyzed to assess the potential impacts of toxic metals in ambient air on the health of residents of Cherokee Heights.

ERG laboratory analysts detected large concentrations of acetaldehyde in canister samples for this VOC monitoring project. ERG recommends sampling for carbonyl compounds in ambient air at Cherokee Heights by means of EPA Compendium Method TO-11A. The CNEP plans to implement such sampling when funding becomes available.

In summary, the CNEP is engaged in a multi-year effort to measure the concentrations of hazardous air pollutants (volatile organic compounds, carbonyl compounds, and metals) in ambient air at the Cherokee Heights tribal housing complex. It has collected eighteen months of data on VOC concentrations; it will begin sampling for metals in fiscal year 2009; and it plans to sample for carbonyl compounds when funding becomes available in the future. The resulting data have been, and will be, analyzed to determine the risks posed by such pollutants to the health of residents of Cherokee Heights.